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Abstract

Thermal expansion measurements were conducted on hot-pressed CrSi₂, TiSi₂, WSi₂ and a two-phase Cr-Mo-Si intermetallic alloy between 293 and 1523 K during three heat-cool cycles. The corrected thermal expansion, $(\Delta L/L_0)_{\text{thermal}}$, varied with the absolute temperature, T, as $(\Delta L/L_0)_{\text{thermal}} = A(T-293)^3 + B(T-293)^2 + C(T-293) + D$, where A, B, C and D are regression constants. Excellent reproducibility was observed for most of the materials after the first heat-up cycle. In some cases, the data from the first heat-up cycle deviated from those determined in the subsequent cycles. This deviation was attributed to the presence of residual stresses developed during processing, which are relieved after the first heat-up cycle.

1.0 Introduction

Intermetallic silicides have found applications as ohmic contacts in the semiconductor industry [1,2,3,4,5], thermoelectric materials [6], heating elements [7,8], protective coatings [9] and they have been proposed for structural applications [10]. A knowledge of the thermal expansion behavior of these silicides is important in these applications in order to reduce or eliminate thermal stresses between the intermetallic silicide and the substrate. Although a compilation of the thermal expansion data on many intermetallic silicides is available [11], the data are fairly old and it is unclear whether they were influenced by impurities and processing methods. Verkhorobin and Matyushenko [12] reported limited data on the coefficients of thermal expansion (CTE) of CrSi₂, MoSi₂, NbSi₂, TaSi₂ and VSi₂ determined from x-ray data. A more complete thermal expansion data on transition metal silicides also determined by x-ray diffraction (XRD) have been reported by Engström and Lönnberg [13]. In contrast, there are only limited thermal expansion data on hot-pressed silicides generated by dilatometric measurements.

The present investigation was undertaken to determine and compare the thermal expansion behavior of hot-pressed CrSi₂, TiSi₂, WSi₂ and a two-phase Cr-Mo-Si intermetallic alloy between 293 and 1523 K by dilatometric measurements.

2.0 Experimental Procedures

Commercially produced powders (–325 mesh) of CrSi₂, TiSi₂, WSi₂ and a Cr-30(at.%)Mo-30%Si¹ alloy were hot-pressed into 25.4 mm long and 9.5 mm in diameter cylindrical specimens at temperatures between 1183 and 1623 K under a pressure 69 to 90 MPa for 0.25 to 4 h under pure argon. The Cr-30%Mo-30%Si alloy was procured from ATI Powder Metals, Pittsburgh, Pennsylvania, as gas atomized powder. Three CrSi₂ specimens were fabricated in separate hot-press runs (582, 619 and 620) in order to evaluate the effect of batch-to-batch variabilities on the thermal expansion data. The two faces of hot-pressed specimens were machined to ensure that they were flat and parallel. The thermal expansion measurements were conducted using a NETZSCH Dilatometer Model DIL 402C² equipped with a high purity alumina as a calibration standard. Measurements were made over three heat-cool cycles to (a)

¹ All compositions are reported in at.% in this paper.

² Trademark of NETZSCH Instruments, North America, LLC, MA.

minimize the effects of compositional, microstructural and processing variables on the data, (b) determine the extent of scatter in the data, and (c) to evaluate a statistical average of the coefficients for the regression curve. The specimen was placed in a sample holder and aligned with a single push-rod with an applied constant load of 0.2 N. The specimens were heated from 293 to 1523 K at 10 K/min. in the first cycle and cooled to 373 K at 10 K/min. in the first cool-down cycle. Subsequent cycles consisted of heating and cooling between 373 and 1523 K. All measurements were conducted in a He atmosphere flowing at 60 cc/min. The length changes were recorded by a computerized data acquisition system. The experimental strain, $\Delta L/L_0$, where ΔL is the differential change in length, $L-L_0$, and L_0 is the original length of the specimen at room temperature, were measured.

3.0 Results and Discussion

3.1 Microstructures

Microstructural observations of the hot-pressed specimens revealed that most of them were well-consolidated although the extent of homogeneity varied from specimen to specimen. Figure 1(a) to (f) show optical micrographs of the transverse cross-sections of three hot-pressed batches of CrSi_2 . While the

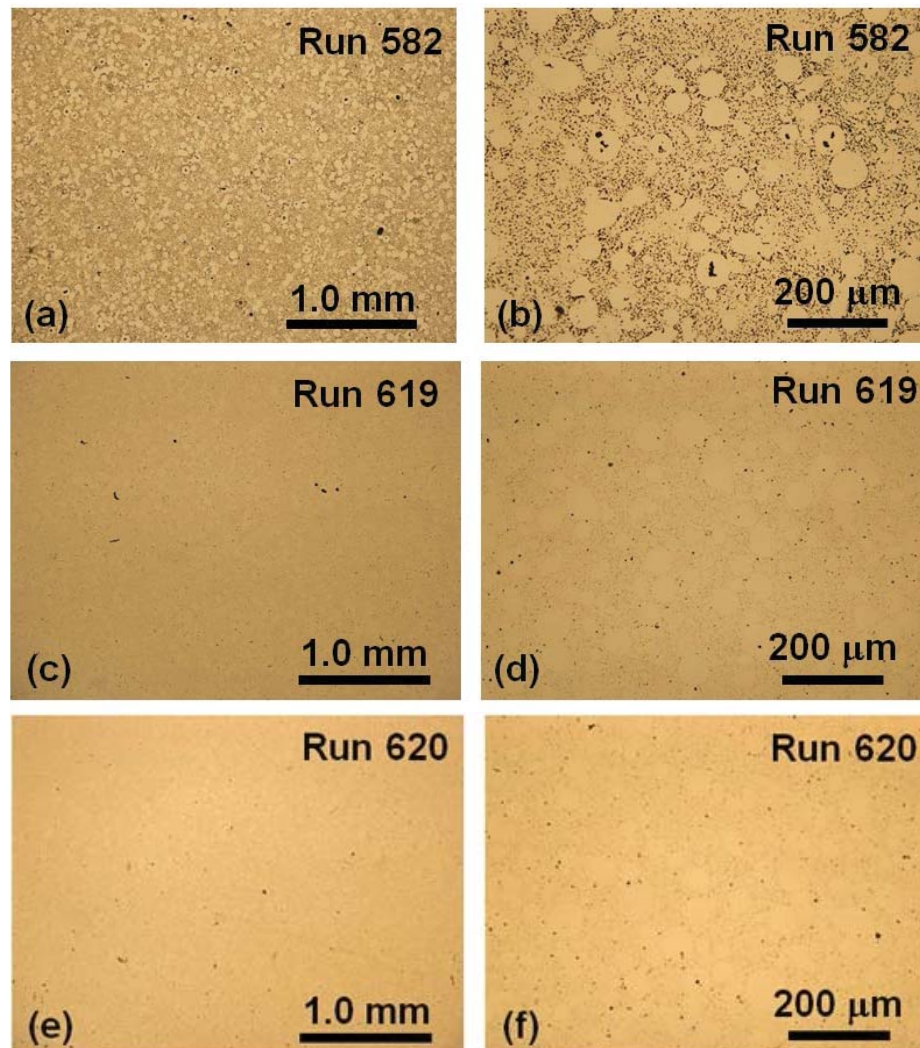


Figure 1.—Low and high magnification optical micrographs of the transverse cross-sections of hot-pressed CrSi_2 specimens fabricated in three runs.

microstructures for specimens from hot-pressing runs 619 and 620 showed a great degree of homogeneity and a distribution of fine grain boundary porosity, the microstructure for run 582 showed the boundaries of the powder particles and extensive porosity. It is noted that run 582 was hot pressed at 1183 K while runs 619 and 620 were hot pressed at 1523 K. The optical microstructures of the hot-pressed Cr-30Mo-30Si alloy were homogeneous and fully consolidated with little porosity (Figure 2(a) to (b)). In contrast, the hot-pressed microstructures of the TiSi_2 (Figure 3(a) to (b)) and WSi_2 (Figure 4(a) to (b)) showed a greater amount of grain boundary porosity.

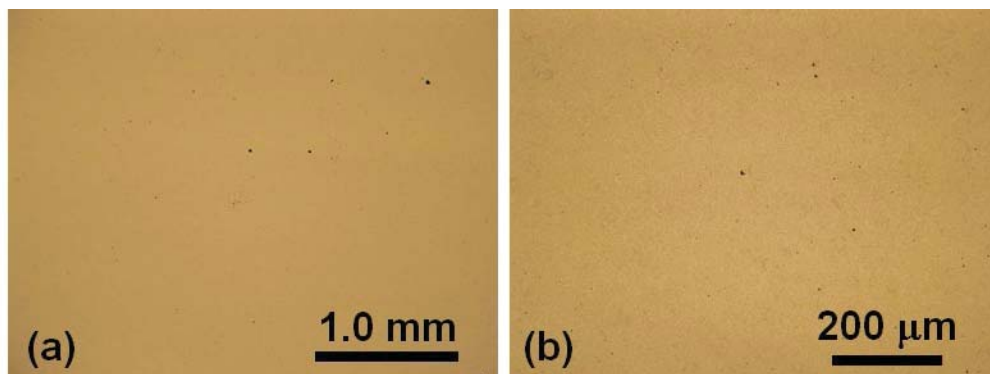


Figure 2.—Low and high magnification optical micrographs of the transverse cross-sections of a hot-pressed Cr-30%Mo-30%Si specimen.

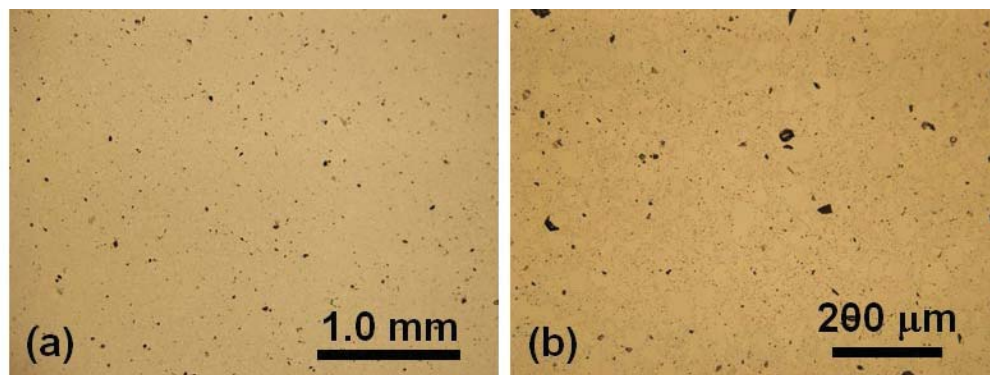


Figure 3.—Low and high magnification optical micrographs of the transverse cross-sections of a hot-pressed TiSi_2 specimen.

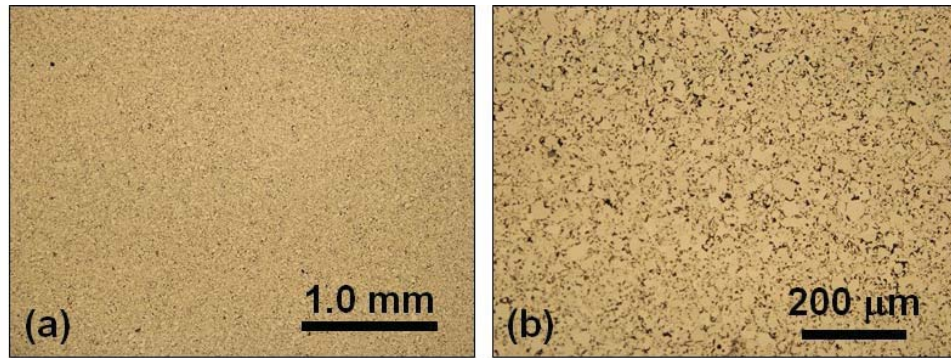


Figure 4.—Low and high magnification optical micrographs of the transverse cross-sections of a hot-pressed WSi₂ specimen.

3.2 Thermal Expansion of CrSi₂

Figure 5(a) to (c) show the variation of the thermal expansion, $(\Delta L/L_0)$, with increasing absolute temperature, T , for the hot-pressed three specimens from runs 582, 619 and 620. On close examination of the results, it is evident that $\Delta L/L_0$ for the first heat-up run is higher than the values for subsequent cool-down and heat-up runs for all three specimens with the difference being more pronounced for run 582. It has been suggested that this discrepancy in the values of $\Delta L/L_0$ between the first and other cool-down and heat-up cycles are due to the relieving of residual stresses developed in the specimens during hot-pressing of the powders during the first heat-up cycle [14]. The measurements from the first cool-down to the third cool-down cycles were fairly reproducible for runs 619 and 620 but a little more scattered for run 582 presumably due to the extensive porosity and heterogeneous microstructure (Figure 1(a) and (b)). Thus, neglecting the data from the first heat-up cycle, the data from the first cool-down to the third cool-down cycles were fitted with Equation (1):

$$(\Delta L/L_0)_{\text{thermal}} = A(T-293)^3 + B(T-293)^2 + C(T-293) + D \quad (1)$$

where, $(\Delta L/L_0)_{\text{thermal}}$ is the magnitude of the $\Delta L/L_0$ without any residual processing strains, A , B , C and D are regression constants. Table I compiles the values of the regression constants and the corresponding coefficients of determination, R_d^2 , for the three CrSi₂ specimens. Figure 6 compares the regression plots for the three specimens, where it is seen that the curves are reasonably close thereby suggesting that batch-to-batch variability is relatively small. Unfortunately, a sparsity of published data on polycrystalline CrSi₂ did permit a meaningful comparison with the present results.

TABLE I.—VALUES OF THE REGRESSION CONSTANTS FOR CRSi₂

Hot press run no.	Cycle description	A, K ⁻³	B, K ⁻²	C, K	D, %	R _d ²
582	First cool-down to third cool-down	2.0×10 ⁻¹⁰	1.2×10 ⁻⁷	1.0×10 ⁻³	-1.8×10 ⁻¹	0.993
619	First cool-down to third cool-down	4.2×10 ⁻¹⁰	-1.4×10 ⁻⁷	1.1×10 ⁻³	-1.4×10 ⁻¹	0.999
620	First cool-down to third cool-down	4.2×10 ⁻¹⁰	-1.8×10 ⁻⁷	1.1×10 ⁻³	-9.3×10 ⁻²	0.999

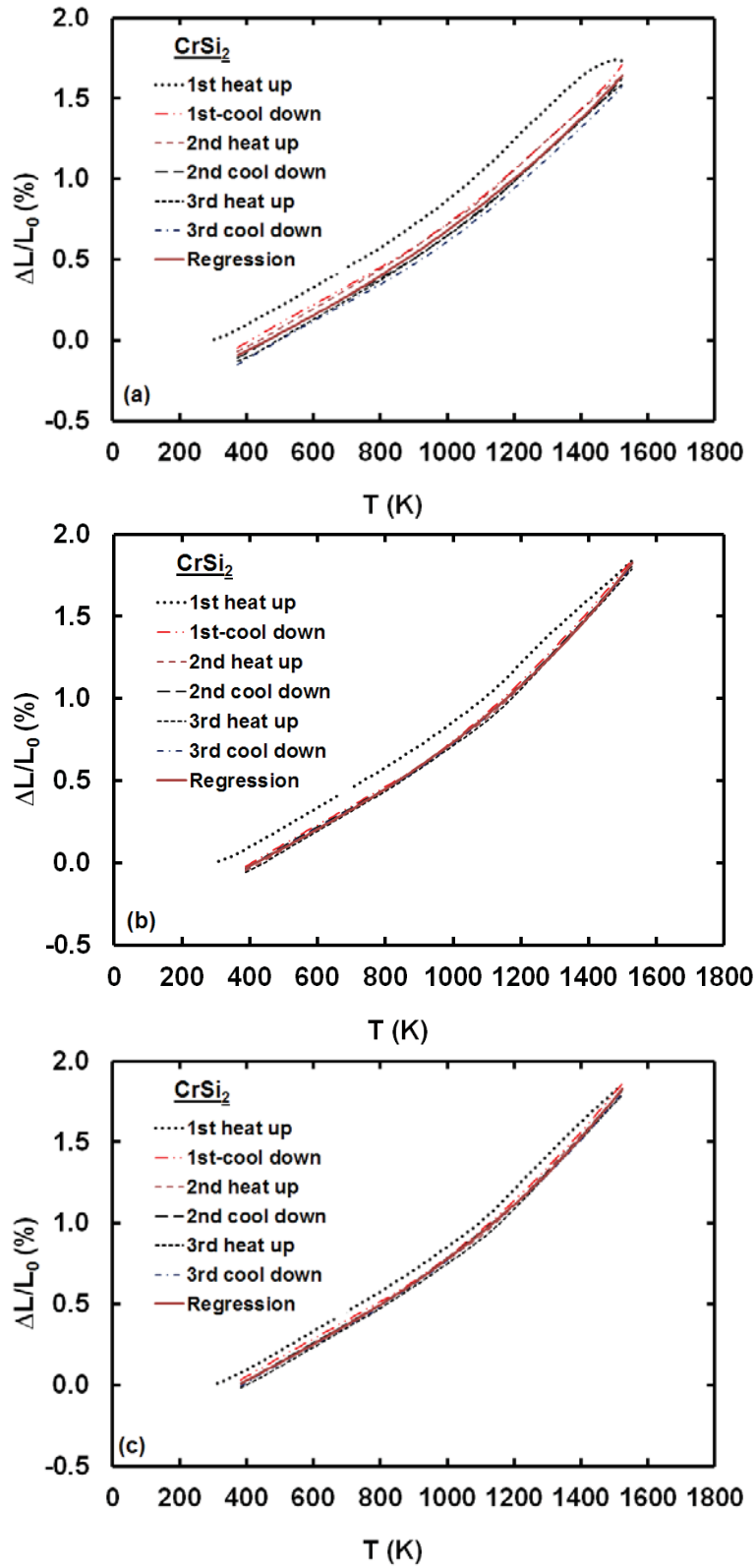


Figure 5.—Temperature dependence of the thermal expansion behavior of CrSi_2 during three heat up-cool down cycles between 293 and 1523 K. The data are shown for three specimens from hot pressed runs (a) 582; (b) 619; and (c) 620.

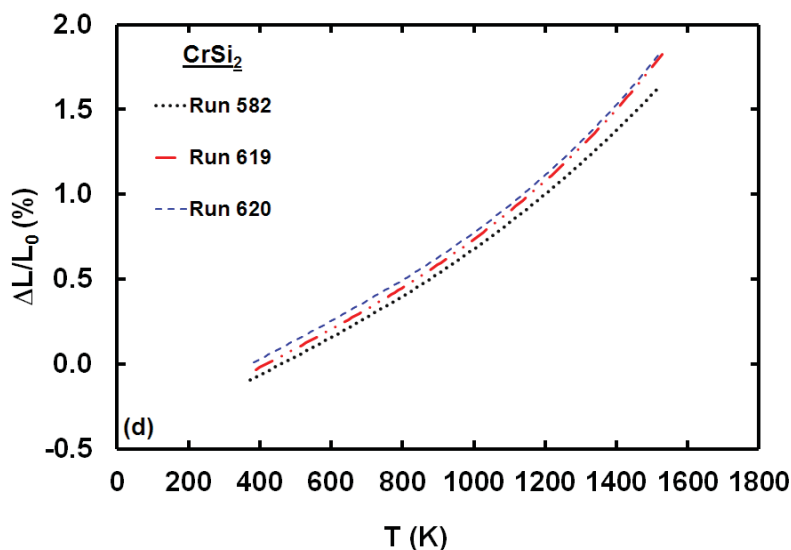


Figure 6.—Comparison of the regression equations for the three CrSi_2 specimens between 293 and 1523 K.

3.3 Thermal Expansion of Cr-30%Mo-30%Si

Figure 7 shows the variation of $\Delta L/L_0$ with increasing T for hot-pressed Cr-30%Mo-30%Si. Unlike the observations on CrSi_2 , the curves almost overlap for all thermal cycles including the first heat-up cycle. This observation suggests that the amount of residual strains developed during hot-pressing of this specimen was negligible. The constants given in Equation (1) were determined by regression analysis of all the data including those measured during the first heat-up cycle. The values of these constants are shown in Table II. Since the Cr-30%Mo-30%Si alloy was prepared by substituting Mo for Cr and Si in Cr_3Si to improve its oxidation resistance [15], published data for Cr_3Si are shown in Figure 8 for comparison [11]. The two sets of data increasingly deviate from each other with increasing temperature, where the deviation is relatively small. It is unlikely that this observed deviation in the thermal expansion can be attributed to the addition of Mo since the microstructure of the Cr-30%Mo-30%Si alloy consists of $(\text{Cr},\text{Mo})_3\text{Si}$ and $(\text{Cr},\text{Mo})_5\text{Si}_3$ [15]. Therefore, this deviation is attributed to experimental scatter.

TABLE II.—VALUES OF THE REGRESSION CONSTANTS FOR Cr-30%Mo-30%Si

Hot press run no.	Cycle description	A, K^{-3}	B, K^{-2}	C, K	D, %	R_d^2
621	First heat-up to third cool-down	1.3×10^{-10}	-1.7×10^{-8}	9.2×10^{-4}	-2.5×10^{-2}	0.9993

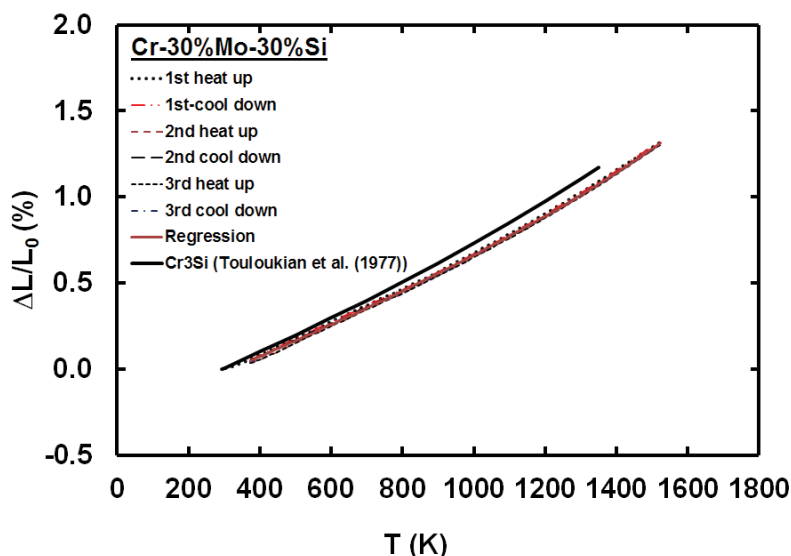


Figure 7.—Temperature dependence of the thermal expansion behavior of Cr-30%Mo-30%Si during three heat up-cool down cycles between 293 and 1523 K. The current results are compared with data for Cr3Si [11].

3.4 Thermal Expansion of TiSi₂

The cyclic thermal expansion characteristics of hot-pressed TiSi₂ are similar to the Cr-30%Mo-30%Si alloy (Figure 8). The curves from the first heat-up to the third cool-down cycle are in excellent agreement with negligible scatter in the data. Once again, it can be concluded that the residual stresses were negligible during hot-pressing of the specimens. Table III gives the values the regression coefficients from the first heat-up to the third cool-down cycle. As shown in Figure 8, the regression line describes the experimental data very well. Comparison of the present results with literature data on TiSi₂ [11] reveals that the two sets of data are in reasonable agreement although they increasingly deviate with increasing temperature.

TABLE III.—VALUES OF THE REGRESSION CONSTANTS FOR TiSi₂

Hot press run no.	Cycle description	A, K ⁻³	B, K ⁻²	C, K	D, %	R _d ²
641	First heat-up to third cool-down	1.8×10 ⁻¹⁰	-1.7×10 ⁻⁷	1.2×10 ⁻³	-2.0×10 ⁻²	0.999

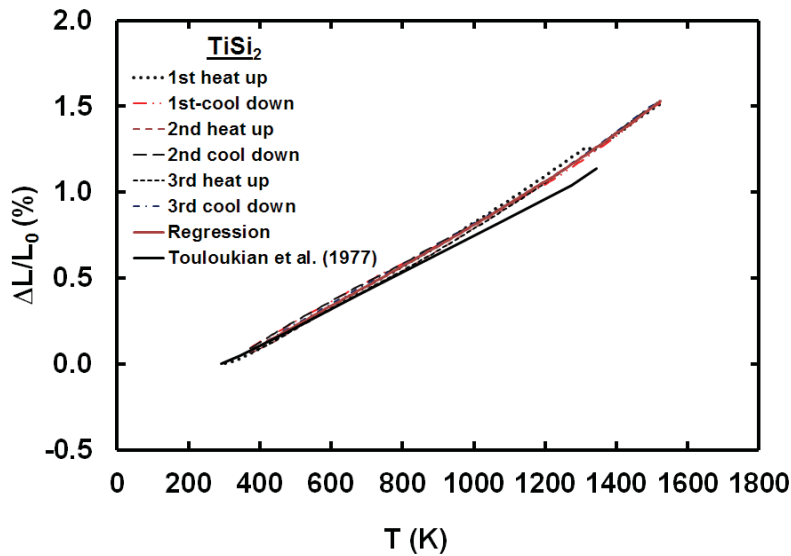


Figure 8.—Temperature dependence of the thermal expansion behavior of TiSi_2 during three heat up-cool down cycles between 293 and 1523 K. The data reported by Touloukian et al. [11] are shown in the figure.

3.5 Thermal Expansion of WSi_2

In contrast to the thermal expansion behavior of the Cr-30%Mo-30%Si alloy (Figure 7) and TiSi_2 (Figure 8), the behavior of WSi_2 is similar to CrSi_2 in that the magnitudes of $\Delta L/L_0$ are larger in the first heat-up cycle than those in the subsequent thermal cycles (Figure 9). However, the difference is smaller than the observations on CrSi_2 (Figure 5(a) to (c)). The regression coefficients for WSi_2 are shown in Table IV, where the data from the first heat-up cycle were not included in the regression analyses. Figure 9 compares the present experimental results with the recommended values for polycrystalline WSi_2 based on calculations from “selected axial thermal expansion values” [11]. Although the latter results are slightly larger than the current experimental regression curve, the two curves are in reasonable agreement with the limits of experimental scatter.

TABLE IV.—VALUES OF THE REGRESSION CONSTANTS FOR WSi_2

Hot press run no.	Cycle description	A, K^{-3}	B, K^{-2}	C, K	D, %	R_d^2
622	First cool-down to third cool-down	1.2×10^{-10}	-1.2×10^{-7}	8.3×10^{-4}	-8.0×10^{-2}	0.999

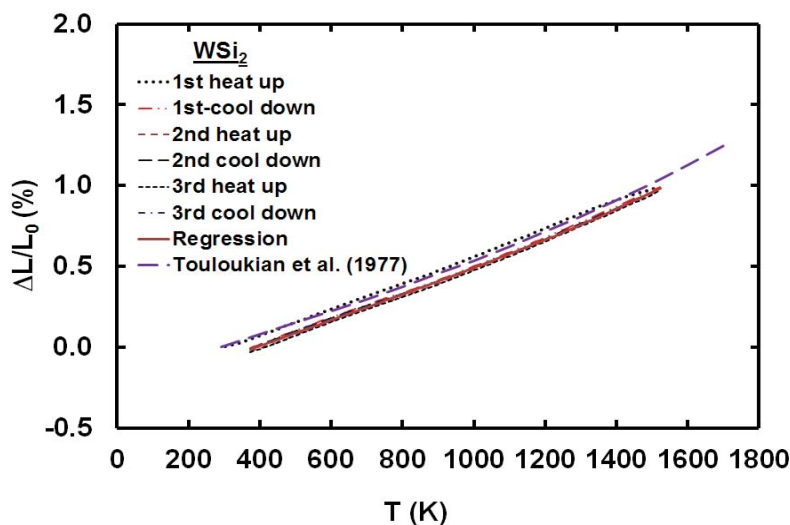


Figure 9.—Temperature dependence of the thermal expansion behavior of WSi_2 during three heat up-cool down cycles between 293 and 1523 K. The present data are compared with those compiled by Touloukian et al. [11].

3.6 Comparison of the Thermal Expansion Behavior of Different Silicides

Metal silicides are used in the semiconductor industry as contact materials [1,2,3,4,5] as well as being considered for other potential applications, such as oxidation-resistant coatings [9] and matrix constituents in SiC fiber-reinforced composite materials [10,16,17,18,19]. Therefore, it is useful to compare the present results with thermal expansion data reported in the literature for MoSi_2 [11], polycrystalline Si [20], SiC [11] and Si_3N_4 [11] (Figure 10). An examination of Figure 10 reveals that the magnitudes of $\Delta L/L_0$ for the metal silicides are higher than those for Si, SiC and Si_3N_4 with the deviation from the latter set of data increasing with increasing temperature. The thermal expansion values are similar for both Si and SiC up to 1000 K but larger than those for Si_3N_4 . While using metal silicide contacts on Si or SiC-based semiconductors are unlikely to debond from the substrate if they operate close to room temperature, Figure 10 suggests that debonding is increasing likely at higher operating temperatures. Similarly, SiC fiber-reinforced silicide matrix composites are likely to develop large thermal strains due to the significant differences in the magnitudes of $\Delta L/L_0$ between the silicides and SiC. Nevertheless, it has been successfully demonstrated that mixing adequate amounts of Si_3N_4 with MoSi_2 to form 0/90 MoSi_2 - Si_3N_4 /SiC_(f) laminated composites lasted over 1000 thermal cycles at 773 K [18].

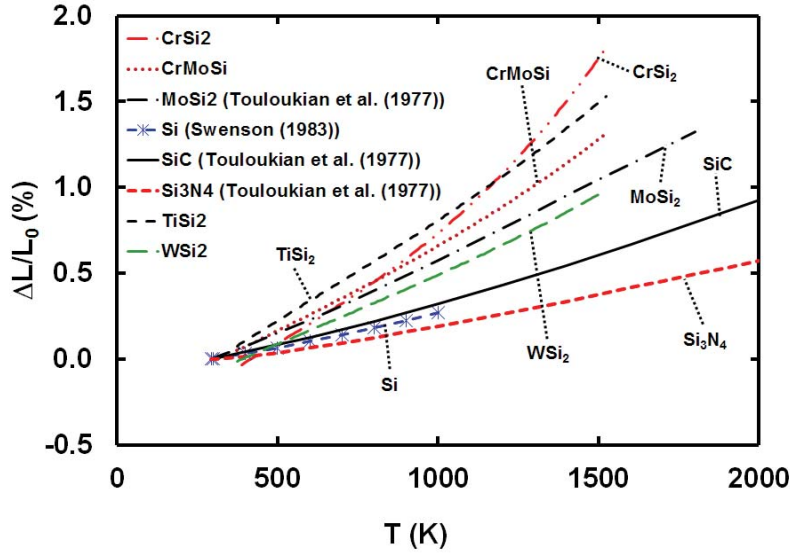


Figure 10.—Comparison of the temperature dependence of the average thermal expansion behaviors of hot-pressed CrSi₂, Cr-30%Mo-30%Si, TiSi₂ and WSi₂ determined in the present investigation with similar data for MoSi₂ [11], Si [20], SiC [11], Si₃N₄ [11], between 293 and 2000 K.

4.0 Summary and Conclusions

Thermal expansion measurements were conducted on hot-pressed CrSi₂, TiSi₂, WSi₂ and a two-phase Cr-Mo-Si intermetallic alloy between 293 and 1523 K during three heat-cool cycles. The optical microstructures of the cross-sections of the hot-pressed specimens revealed that they were well consolidated except in the case of one CrSi₂ specimen, where there was a large amount of grain boundary porosity. Batch-to-batch comparisons with measurements made on two other CrSi₂ specimens revealed that the values of $\Delta L/L_0$ for this specimen were slightly lower. Unlike for the other materials investigated in the present research, the first heat-up cycle data for the CrSi₂ and WSi₂ deviated from those determined in the subsequent cycles due to the presence of residual stresses developed during processing. Once these stresses were relieved after the first heat-up cycle, the data generated in the second and third heat-up and cool-down cycles were in excellent agreement. The magnification of, $(\Delta L/L_0)_{\text{thermal}}$, varied with T as

$$(\Delta L/L_0)_{\text{thermal}} = A(T-293)^3 + B(T-293)^2 + C(T-293) + D$$

where, A, B, C and D are regression constants.

The present data were compared with those reported for MoSi₂ [11], Si [20], SiC [11] and Si₃N₄ [11]. It is demonstrated that the thermal expansion for the silicides were larger than those for Si, SiC and Si₃N₄ with the deviation between the former and latter set of data increasing with increasing temperature. It is concluded that the thermal strains would increase with increasing temperature if silicides are used as contact materials on Si or SiC, or in silicide-based SiC fiber reinforced composites.

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